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DBU-mediated [4 + 2] annulations of donor–acceptor cyclopropanes with 3-aryl-2-cyanoacrylates for the synthesis of fully substituted anilines†

Jiaming Liu, Siran Qian, Zhenjie Su and Cunde Wang *

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A facile synthesis of fully substituted anilines by the DBU-mediated [4 + 2] annulation of donor–acceptor 1,1-dicyano-cyclopropanes with 3-aryl-2-cyanoacrylate has been developed. This reaction involves a highly efficient multiple domino sequence consisting of ring opening of donor–acceptor cyclopropanes, regioselective intermolecular Michael addition, intramolecular nucleophilic addition and aromatization as key unit steps. This transformation provides a straightforward synthetic protocol for constructing fully substituted aniline derivatives. The structure of two typical products was confirmed by X-ray crystallography.

Polysubstituted benzenes are very valuable intermediates in the synthesis of numerous natural products and synthetic pharmaceuticals.[1] Among polysubstituted benzene derivatives, those containing nitrogen-substituted benzene derivatives as a privileged scaffold have attracted more attention recently and serve as the central pharmacophore in drug discovery. These molecules were investigated extensively as neuraminidase inhibitors,[2] antimicrobial agents,[3] and biochemical fluorescent agents.[4]

As a result of the unique photophysical and electronic properties, polysubstituted benzenes also were utilized as a versatile synthetic building block in materials science and continue to draw the interest of a large segment of the scientific community.[5] Researchers have shown that polysubstituted benzenes have important fluorescence properties in solution and in the solid state which can play a significant role in optical and electronic devices such as organic lasers, light-emitting diodes (OLEDs), and organic field-effect transistors (OFET).[6] Additionally, polysubstituted benzene derivatives also were used to construct the molecular architecture of MOF family and liquid crystals.[7] Given their immense pharmaceutical and material usefulness, the development of efficient syntheses of these polysubstituted benzene derivatives has thus attracted many medicinal and material chemists for decades. Traditionally, there were several methods for the preparation of the polysubstituted benzene derivatives including electrophilic or nucleophilic substitutions of benzene ring, coupling reactions catalyzed by transition metals,[8] and metalation functionalization reactions.[9]

Later, cycloaddition or annulation of suitable acyclic precursors has drawn great attention for the structure of polysubstituted benzenes such as the [3 + 2 + 1] Dötz reaction,[10] [3 + 3] cyclocondensation,[11] [4 + 2] annulations,[12] [5 + 1] benzannulation of alkenoyl ketene-acetals and nitroalkane.[13] Recently, Xin and co-workers described an appealing strategy to directly construct polysubstituted benzenes *via* sequential Michael addition, Knoevenagel condensation and nucleophilic cyclization reactions of chalcones with active methylene compounds in guanidinium ionic liquids.[14] In the same way, using L-proline as a catalyst in an ionic liquid, the sequential Michael addition and cyclocondensation of arylethylidenemalononitriles with arylidenemalononitriles also afforded polyfunctionalized benzenes.[15] In addition, multicomponent reactions as an efficient synthetic strategy have drawn considerable attention over the past decades, because complex products are formed in a one-pot reaction and diversity can be simply attained by relatively simple starting materials. One-pot multicomponent reactions for the construction of structurally and stereochemically diverse polysubstituted benzenes has been developed using varies catalysts such as biodegradable cellulose sulfuric acid,[4] reusable silica nanoparticles,[16] *N*,*N*-dimethyl-4-aminopyridine (DMAP).[17]

In recent years, as useful three-carbon synthons, cyclopropanes with donor and acceptor substituents in the vicinal positions (D–A cyclopropanes) have drawn considerable attention from synthetic chemists. D–A cyclopropanes easily underwent a variety of ring-opening reactions under the influence of a variety of conditions to form 1,3-dipolarophiles, which were

School of Chemistry and Chemical Engineering, Yangzhou University, 180 Siwangting Street, Yangzhou 225002, P. R. China. E-mail: wangcd@yzu.edu.cn; Fax: +86-514-8797-5244; Tel: +86-514-8797-5568

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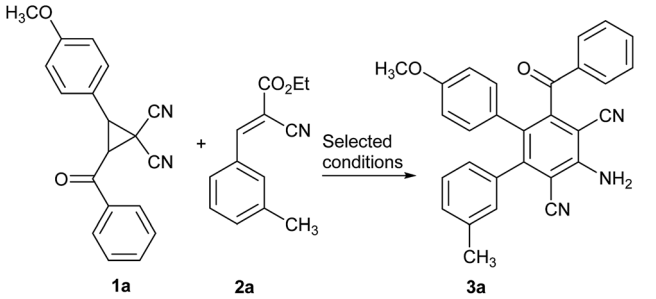
employed to react with a variety of dipolarophiles such as carbonyls, alkenes, imines, nitriles, and nitrones to construct varied important heterocycles.[18] In addition, D–A cyclopropanes as appropriate candidates also underwent cyclodimerization in the absence of dipolarophiles or other reagents.[19] Very recently, our group disclosed an efficient and straightforward synthetic protocol for the preparation of fully substituted benzenes *via* a [3 + 3]-cyclodimerization reaction of 1-cyanocyclopropane 1-esters.[11c]

Owing to that 2,6-dicyanoanilines belong to typical acceptor–donor–acceptor (A–D–A) systems, which are the basis for artificial photosynthetic systems, materials possessing semiconducting or nonlinear properties, and molecular electronic devices.[20] The development of methodologies for a direct access to highly substituted and specifically functionalized 2,6-dicyanoanilines is a continuing challenge in modern synthetic organic chemistry.

In continuation of our interests in D–A cyclopropanes and constructing cyclic compounds, based on our studies on the reactivity of 2-aroyl-3-aryl-1-cyanocyclopropane-1-carboxylates,[21] we envisioned that the reaction of D–A 1,1-dicyanocyclopropanes which supply three carbons from the skeleton of cyclopropane and other carbon from its cyano group with substituted 3-aryl-2-cyanoacrylates may offer an efficient approach to benzene skeletons *via* [4 + 2] annulations and aromatization. To the best of our knowledge, no example using [4 + 2] annulations of D–A 1,1-dicyanocyclopropanes as starting materials to construct the 2,6-dicyanoaniline core were reported. In this context, the [4 + 2] annulations of D–A 1,1-dicyanocyclopropanes with substituted 3-aryl-2-cyanoacrylates could provide an easy access to highly substituted 2,6-dicyanoaniline frameworks.

Based on our more recent results,[21] the donor–acceptor 1,1-dicyanocyclopropanes was easily promoted by basic agents to form a 1,3-dipole, the following 2-aroyl-1,1-dicyano-3-arylprop-2-en-1-ide anion generated *via* removal of a proton, which could attack an electron-defect double or triple bond as a nucleophilic agent.[21] The reaction was carried out firstly by stirring the mixture of 2-benzoyl-3-(4-methoxyphenyl) cyclopropane-1,1-dicarbonitrile (**1a**), ethyl 2-cyano-3-(*m*-tolyl) acrylate (**2a**) and Et_3N in dichloromethane at 20 °C for 24 h, the desired product was not obtained (Table 1, entry 1). Then, reaction of cyclopropane-1,1-dicarbonitrile **1a** and 2-cyanoacrylate **2a** using Et_3N in dichloromethane resulted in the formation of 2,6-dicyanoaniline **3a** in only 29% at 40 °C after 24 h (Table 1, entry 2). Exploring the effect of various bases, DBU, DABCO, piperidine, and NaOH were employed under similar reaction conditions (entries 3–6). Pleasingly, DBU and DABCO gave decent yields of 2,6-dicyanoaniline **3a** (entries 3–4). Using piperidine as a base, only 5% of 2,6-dicyanoaniline **3a** were obtained (entry 5), and in the presence of NaOH, no reaction took place (entry 6). Considering the replacement of dichloromethane by 1,2-DCE, toluene, and DMF for the raising of reaction temperature, the changing the solvent to 1,2-DCE instead of dichloromethane at 40 °C, 70 °C and 80 °C, respectively, did not have a significant improvement (entries 7–9), however, the results indicated the important role of the reaction

Table 1 Optimization of reaction conditions in the synthesis of **3a**[a]



1a **2a** **3a**

Entry	Base	Solvent	T (°C)	t (h)	Yield[b] (%)
1	Et_3N (1.0)	DCM	20	24	0
2	Et_3N (1.0)	DCM	40	24	29
3	DBU (1.0)	DCM	40	10	90
4	DABCO (1.0)	DCM	40	12	75
5	Piperidine (1.0)	DCM	40	24	<5
6	NaOH (1.0)	DCM	40	12	0
7	DBU (1.0)	1,2-DCE	40	12	48
8	DBU (1.0)	1,2-DCE	70	10	75
9	DBU (1.0)	1,2-DCE	80	10	86
10	DBU (1.0)	Toluene	40	12	43
11	DBU (1.0)	Toluene	100	10	85
12	DBU (1.0)	Toluene	110	9	83
13	DBU (1.0)	DMF	40	24	Trace
14	DBU (1.0)	DMF	100	24	Trace
15	DBU (1.25)	DCM	40	9	90
16	DBU (0.75)	DCM	40	14	85

[a] Reaction conditions: 1 mmol of **1a**, 1.2 equiv. of **2a**, appropriate basic reagent, 15 mL solvent. [b] Isolated yield.

temperature, the higher temperature was propitious to the formation of 2,6-dicyanoaniline **3a**. The aforementioned experiments showed that both toluene and DMF play crucial roles in generating the 1,3-dipole from donor–acceptor cyclopropanes. In order to improve the yield of product **3a**, switching the solvent to toluene or DMF did not give the best yields of the desired product **3a** under high-temperature conditions, indicating the important role of the solvent and reaction temperature (entries 10–14). It was worth mentioning at this point that in DMF, the desired product **3a** was obtained hardly any, but the formation of 3,6-bisbenzoyl-4,5-bis(4-methoxyphenyl) phthalonitrile was observed *via* [3 + 3] dimerization of cyclopropane-1,1-dicarbonitrile **1a**, which was consistent with our previous reports.[11c] However, higher loading of DBU (to 1.25 equiv.) under otherwise identical conditions did not significantly improve the yield of 2,6-dicyanoaniline **3a**, the reaction time was shortened slightly (entry 15). Subsequently, reducing the amount of DBU from 1.0 equiv. to 0.75 equiv. gave the expected product **3a** in 85% yield (Table 1, entry 16), lower than that yield of product **3a** using 1.0 equiv. DBU, furthermore the longer reaction time was needed.

A series of experiments revealed that the optimal results were obtained when the reaction of 2-benzoyl-3-(4-methoxyphenyl)-cyclopropane-1,1-dicarbonitrile (**1a**) and 1.2 equiv. ethyl

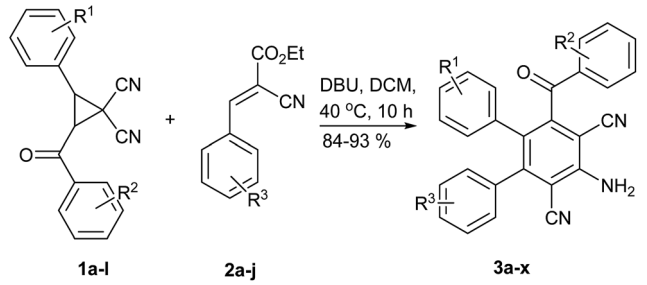
2-cyano-3-(*m*-tolyl)acrylate (**2a**) together with 1.0 equiv. DBU was carried out in dichloromethane, the resultant mixture was stirred for 10 h at 40 °C, whereby the yield of product **3a** reached 90% (Table 1, entry 3).

Under the optimized conditions as described in entry 3, Table 1, the generality of the reaction was examined in Table 2. The reaction tolerates different substituents on the 1,1-dicyanocyclopropanes and substituted 3-aryl-2-cyanoacrylates, generally, 1,1-dicyanocyclopropanes with a range of substituents at aryl such as methoxy, methyl, chloro, and bromo groups all worked well to give 2,6-dicyanoaniline derivatives. Substrate 3-aryl-2-cyanoacrylates at aryl with electron-withdrawing group such as chloro, bromo, fluoro and ester gave the products in higher yields than the aryl with electron-donating methoxy and methyl. The electronic properties and positions of the substituents on the benzene ring of 3-aryl-2-cyanoacrylates had a slight effect on the reaction. Additionally, substrate 3-aryl-2-cyanoacrylate with a heterocycle such as thiophene also worked well to give the corresponding products. The molecular structures of all 2,6-dicyanoanilines **3a–x** were elucidated from their spectroscopic analyses as described herein for **3a**. In the IR spectrum of **3a**, two sharp absorption bands at 2221 and 1665 cm^{-1} could be related to *CN* and Ph*CO*Ar stretching frequencies. The high-resolution mass spectrum of **3a** displayed the molecular ion peak at m/z = 466.1530 [(M + Na)$^+$], which is in good agreement with the proposed structure. The ^{1}H NMR spectrum of **3a** exhibited three sharp singlet signals at 5.31 ppm (bs, 2H), 3.52 ppm (s, 3H), 2.17 ppm (s, 3H) for Ar–*NH*$_2$, ArO*CH*$_3$ and Ar*CH*$_3$, respectively. Characteristic ^{1}H chemical shift of Ar–NH_2, $ArOCH_3$ and $ArCH_3$ unequivocally indicated the exclusive chemical environment of 2,6-dicyanoaniline **3a** protons. The ^{1}H-decoupled ^{13}C NMR spectrum of **3a** showed 24 distinct signals in agreement with the suggested structure. The important peaks were related to the Ar*C*O, CO*CH*$_3$, and Ph*CH*$_3$ groups which appeared at = 193.4, 54.1, and 20.4 ppm (see ESI†).

Final confirmation for the formation of the reaction products was obtained by X-ray crystal structure analysis of compounds **3b** and **3i**. The structures of **3b** and **3i** was unambiguously solved by X-ray crystallography (Fig. 1).[22] X-ray crystallographic analysis determined that products **3b** and **3i** possess two aryl and an aroyl contiguous substituents at C(3), C(4) and C(5) of 2,6-dicyanoaniline core.

Based on the above experimental results, a possible mechanism is proposed in Scheme 1. Initially, the cyclopropane was activated by base generated a zwitterions [**A**], which formed easily 2-aroyl-1,1-dicyano-3-arylprop-2-en-1-ide [**B**].[21] The Michael addition of 2-aroyl-1,1-dicyano-3-arylprop-2-en-1-ide [**B**] to the substrate ethyl 3-aryl-2-cyanoacrylate afforded the intermediate 5-aroyl-2,6,6-tricyano-1-ethoxy-1-oxo-3,4-diarylhex-5-en-2-ide [**C**]. Subsequently, the intramolecular nucleophilic addition of intermediate [**C**] to C6-cyano group formed the intermediate 6′-aroyl-3′,5′-dicyano-4′-imino-1′,2′,3′,4′-tetrahydro-[1,1′:2′,1″-terphenyl]-3′-carboxylate [**D**] again, which transferred easily to the intermediate enamine ethyl 4′-amino-6′-aroyl-3′,5′-dicyano-2′,3′-dihydro-[1,1′:2′,1″-terphenyl]-3′-carboxylate [**E**] in the presence of base DBU *via* 1,5-H shift. The following base DBU-promoted the tautomerism of the intermediate [**E**] gave the intermediate 4′-amino-2′,3′-dihydro-[1,1′:2′,1″-terphenyl]-3′-carboxylate [**F**].

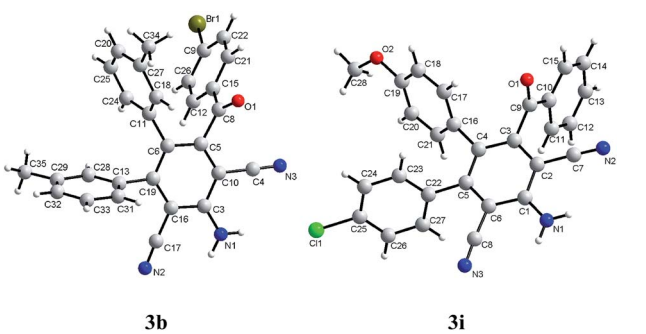
Table 2 Scope with respect to D–A cyclopropanes and 2-cyanoacrylates[a]



1a-l 2a-j 3a-x

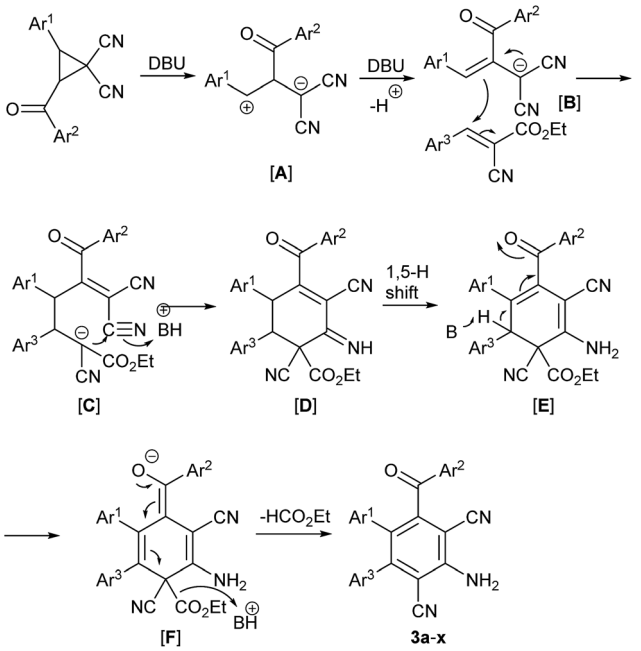
Entry	R^1	R^2	R^3	Yield[b] (%)
1	*p*-CH_3O	H	*m*-CH_3	90 (**3a**)
2	*m*-CH_3	*p*-Br	*m*-CH_3	90 (**3b**)
3	*m*-CH_3	*p*-Br	*p*-CH_3O	87 (**3c**)
4	*m*-CH_3	*p*-Br	*p*-Cl	91 (**3d**)
5	*m*-CH_3	*p*-Br	*p*-Br	92 (**3e**)
6	*m*-CH_3	*p*-Br	*o*-CH_3	89 (**3f**)
7	*p*-Cl	H	*m*-CH_3	89 (**3g**)
8	*p*-Cl	H	*p*-Br	92 (**3h**)
9	*p*-CH_3O	H	*p*-Cl	90 (**3i**)
10	*p*-CH_3O	*p*-Br	*p*-Cl	88 (**3j**)
11	*m*-Cl	*m*-CH_3	*m*-Cl	93 (**3k**)
12	*m*-Cl	*m*-CH_3	*p*-Br	92 (**3l**)
13	*p*-Cl	*m*-CH_3	*p*-CH_3	89 (**3m**)
14	*m*-CH_3	H	*m*-Br	91 (**3n**)
15	*m*-CH_3	H	Thiophen-2-	84 (**3o**)
16	*m*-CH_3	H	*m*-Cl	89 (**3p**)
17	*m*-CH_3	*m*-CH_3	*m*-Cl	91 (**3q**)
18	*p*-CH_3O	*m*-CH_3	*o*-CH_3	88 (**3r**)
19	*m*-CH_3	*m*-CH_3	*p*-Cl	90 (**3s**)
20	*m*-Cl[c]	*m*-CH_3	Thiophen-2-	86 (**3t**)
21	*p*-Cl	H	3,5-$Cl_2C_6H_4$	93 (**3u**)
22	*m*-CH_3	H	*p*-PhO	88 (**3v**)
23	*p*-CO_2CH_3	*m*-CH_3O	*m*-CH_3	84 (**3w**)
24	*p*-F	*m*-CH_3O	*m*-CH_3	89 (**3x**)

[a] Reaction conditions: substituted 1,1-dicyanocyclopropanes **1a–k** (1 mmol), substituted 3-aryl-2-cyanoacrylates **2a–k** (1.2 mmol), DBU (152 mg, 1.0 mmol), dichloromethane (15 mL), 40 °C, 10 h. [b] Isolated yield. [c] Ethyl-2-cyano-3-(thiophen-2-yl)acrylate was used as a substrate 3-aryl-2-cyanoacrylate.



3b 3i

Fig. 1 Molecular structure of 2,6-dicyanoanilines **3b** and **3i**.



Scheme 1 Tentative reaction mechanism.

The fully substituted benzenes were finally obtained through the aromatization of the intermediate 4′-amino-2′,3′-dihydro-[1,1′:2′,1″-terphenyl]-3′-carboxylate [**F**] by removal of ethyl formate in the presence of base DBU.[11c,23]

Conclusions

In conclusion, we have developed an efficient DBU-mediated [4 + 2] annulations of donor–acceptor 1,1-dicyanocyclopropanes with ethyl 3-aryl-2-cyanoacrylate for the preparation of fully substituted anilines which are a wide range of structurally interesting and pharmacologically significant compounds. This reaction involves a highly efficient multiple domino sequence consisting of ring opening of donor–acceptor cyclopropanes, regioselective intermolecular Michael addition, intramolecular nucleophilic addition and aromatization as key unit steps. The reaction appears to be general for a variety of 1,1-dicyanocyclopropanes and 3-aryl-2-cyanoacrylate and tolerates the presence of aromatic moieties with electron-withdrawing and electron-donating substituents. It should be pointed out that this transformation presents a novel synthetic protocol, which is complementary and superior to previous synthetic methods for the formation of fully substituted aniline derivatives.

Experimental section

All melting points were determined in a Yanaco melting point apparatus and are uncorrected. IR spectra were recorded in a Nicolet FT-IR 5DX spectrometer. The ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded in a Bruker AV-400 spectrometer with TMS as internal reference in $CDCl_3$ solutions. The *J* values are given in hertz. Only discrete or characteristic signals for the ^{1}H NMR are reported. High-resolution ESI mass spectra were obtained on a UHR-TOF maXis (ESI) mass spectrometer. X-ray crystallographic analysis was performed with a SMART APEX-II diffractometer. Flash chromatography was performed on silica gel (230–400 mesh) eluting with ethyl acetate–hexanes mixture. All reactions were monitored by thin layer chromatography (TLC). All reagents and solvents were purchased from commercial sources and purified commonly before used.

The standard procedure for the synthesis of fully substituted anilines *via* [4 + 2] reaction between substituted 2-aroyl-3-arylcyclopropane-1,1-dicarbonitriles and 3-aryl-2-cyanoacrylates as follows.

To the mixture of 2-aroyl-3-arylcyclopropane-1,1-dicarbonitriles **1a–k** (1.0 mmol) and 3-aryl-2-cyanoacrylates **2a–k** (1.2 mmol) in dichloromethane (15 mL) was added DBU (152 mg, 1.0 mmol) at room temperature, and the resultant mixture was stirred at room temperature for 5 min. The resulting mixture was stirred at 40 °C for 10 h, and the completion of reaction was confirmed by TLC (hexanes/EtOAc, 6/1). Subsequently, the resultant mixture was added with water (10 mL) and the water phase was extracted with dichloromethane (15 mL). The combined organic phase was washed with water (5 mL) and brine (5 mL), and dried over anhydrate sodium sulfate. After removal of dichloromethane, the crude product was purified by flash chromatography (silica gel, EtOAc/hexanes, 1/10) to give the desirable products **3a–x.**

4′-Amino-6′-benzoyl-4-methoxy-3″-methyl-[1,1′:2′,1″-terphenyl]-3′,5′-dicarbonitrile (3a)

Yellow solid, yield: 90%; mp 205.0–205.8 °C (EA/PE); IR (KBr, cm^{-1}): ν 3421, 3323, 3236, 2221, 1665, 1639, 1481, 1255, 931, 825, 751; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.53 (d, $J = 6.6$ Hz, 2H), 7.40 (s, 1H), 7.24 (s, 2H), 7.13–6.92 (m, 2H), 6.92–6.71 (m, 2H), 6.59 (s, 1H), 6.36 (s, 2H), 5.31 (s, 2H), 3.52 (s, 3H), 2.17 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 193.4, 157.8, 150.2, 149.9, 147.3, 137.0, 135.1, 134.5, 133.3, 131.2, 129.2, 128.7, 128.1, 127.7, 127.2, 126.3, 125.7, 114.3, 113.4, 112.3, 98.6, 93.1, 54.1, 20.4; HR-MS (ESI) calcd for $C_{29}H_{21}N_3O_2$ [(M + Na)$^+$]: 466.1531; found: 466.1530.

4′-Amino-6′-(4-bromobenzoyl)-3,3″-dimethyl-[1,1′:2′,1″-terphenyl]-3′,5′-dicarbonitrile (3b)

White solid, yield: 90%; mp 229.9–230.5 °C (EA/PE); IR (KBr, cm^{-1}): ν 3441, 3332, 3231, 2221, 1673, 1649, 1457, 1253, 1201, 1174, 900, 835, 812; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.37 (s, 4H), 7.10–6.92 (m, 2H), 6.84 (s, 2H), 6.76–6.59 (m, 2H), 6.47 (s, 2H), 5.35 (s, 2H), 2.15 (s, 3H), 1.93 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 193.1, 150.9, 150.8, 147.2, 137.8, 137.8, 137.3, 135.6, 134.6, 134.2, 131.8, 131.5, 130.7, 129.9, 129.4, 128.2, 127.9, 127.8, 127.5, 126.4, 115.1, 114.1, 110.0, 99.6, 93.8, 21.2, 20.9; HR-MS (ESI) calcd for $C_{29}H_{20}BrN_3O$ [(M + Na)$^+$]: 528.0687; found: 528.0692.

4′-Amino-6′-(4-bromobenzoyl)-4″-methoxy-3-methyl-[1,1′:2′,1″-terphenyl]-3′,5′-dicarbonitrile (3c)

Yellow solid, yield: 87%; mp 226.8–227.4 °C (EA/PE); IR (KBr, cm^{-1}): ν 3453, 3336, 3203, 2215, 1678, 1638, 1446, 1244, 1232,

1170, 900, 816, 822; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.43 (s, 3H), 7.25 (s, 1H), 7.03 (d, J = 7.9 Hz, 2H), 6.83–6.70 (m, 4H), 6.54 (s, 1H), 6.50 (d, J = 6.1 Hz, 1H), 5.37 (s, 2H), 3.75 (s, 3H), 2.01 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 192.1, 158.9, 149.9, 149.5, 146.2, 136.4, 133.8, 133.2, 130.8, 130.5, 129.9, 129.7, 128.7, 128.4, 127.2, 126.9, 126.7, 114.2, 113.1, 112.6, 98.7, 92.7, 54.1, 20.0; HR-MS (ESI) calcd for $C_{29}H_{20}BrN_3O_2$ [(M + Na)$^+$]: 544.0637; found: 544.0639.

4′-Amino-6′-(4-bromobenzoyl)-4″-chloro-3-methyl-[1,1′:2′,1″-terphenyl]-3′,5′-dicarbonitrile (3d)

Yellow solid, yield: 91%; mp 213.5–214.0 °C (EA/PE); IR (KBr, cm^{-1}): ν 3447, 3338, 3239, 2225, 1671, 1647, 1419, 1258, 928, 829, 759; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.42–7.29 (m, 4H), 7.19–7.10 (m, 2H), 6.99 (d, J = 7.7 Hz, 2H), 6.81–6.69 (m, 2H), 6.53–6.37 (m, 2H), 5.37 (s, 2H), 1.96 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 192.3, 150.3, 148.7, 146.9, 137.1, 134.6, 133.7, 133.6, 133.5, 131.3, 130.8, 130.1, 130.1, 129.5, 129.0, 127.9, 127.3, 127.2, 114.2, 113.3, 98.9, 94.4, 20.4; HR-MS (ESI) calcd for $C_{28}H_{17}BrClN_3O$ [(M + Na)$^+$]: 548.0141; found: 548.0140.

4′-Amino-4″-bromo-6′-(4-bromobenzoyl)-3-methyl-[1,1′:2′,1″-terphenyl]-3′,5′-dicarbonitrile (3e)

White solid, yield: 92%; mp 222.5–223.6 °C (EA/PE); IR (KBr, cm^{-1}): ν 3449, 3353, 3227, 2220, 1679, 1635, 1447, 1248, 901, 852, 758; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.48–7.34 (m, 6H), 6.98 (d, J = 7.6 Hz, 2H), 6.78–6.68 (m, 2H), 6.62–6.41 (m, 2H), 5.41 (s, 2H), 2.02 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 192.8, 150.8, 149.2, 147.5, 137.6, 134.6, 134.2, 134.0, 131.8, 131.4, 131.4, 130.9, 130.6, 129.6, 129.5, 128.5, 127.8, 127.8, 123.5, 114.8, 113.8, 99.3, 94.4, 21.0; HR-MS (ESI) calcd for $C_{28}H_{18}Br_2N_3O$ [(M + Na)$^+$]: 593.9616; found: 593.9630.

4′-Amino-6′-(4-bromobenzoyl)-2″,3-dimethyl-[1,1′:2′,1″-terphenyl]-3′,5′-dicarbonitrile (3f)

Yellow solid, yield: 89%; mp 231.6–232.4 °C (EA/PE); IR (KBr, cm^{-1}): ν 3419, 3356, 3227, 2210, 1674, 1656, 1438, 1235, 910, 873, 782; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.37 (s, 4H), 7.15–7.06 (m, 1H), 7.14–7.01 (m, 3H), 6.70–6.68 (m, 2H), 6.48 (s, 2H), 5.32 (s, 2H), 1.97 (s, 3H), 1.92 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 193.1, 151.0, 150.6, 147.1, 137.2, 135.4, 135.0, 134.4, 134.2, 131.8, 130.6, 130.2, 129.9, 129.4, 129.3, 129.1, 128.4, 127.4, 125.5, 114.5, 114.0, 100.2, 94.4, 21.0, 19.7; HR-MS (ESI) calcd for $C_{29}H_{20}BrN_3O$ [(M + Na)$^+$]: 528.0687; found: 528.0696.

4′-Amino-6′-benzoyl-4-chloro-3″-methyl-[1,1′:2′,1″-terphenyl]-3′,5′-dicarbonitrile (3g)

Yellow solid, yield: 89%; mp 210.5–211.2 °C (EA/PE); IR (KBr, cm^{-1}): ν 3448, 3325, 3226, 2219, 1672, 1638, 1445, 1249, 926, 863, 763; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.53 (d, J = 7.6 Hz, 2H), 7.44 (dd, J = 6.9 Hz and 6.9 Hz, 1H), 7.27 (dd, J = 7.3 Hz and 7.3 Hz, 2H), 7.09–6.96 (m, 2H), 6.82 (d, J = 8.4 Hz, 4H), 6.64 (d, J = 7.0 Hz, 2H), 5.38 (s, 2H), 2.17 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 192.8, 150.0, 149.8, 146.9, 137.0, 134.4, 134.1, 133.4, 132.5, 132.5, 131.0, 128.9, 128.7, 128.5, 127.6, 127.2, 126.9, 125.4, 113.9, 113.0, 98.5, 93.0, 20.2; HR-MS (ESI) calcd for $C_{28}H_{18}ClN_3O$ [(M + Na)$^+$]: 470.1036; found: 470.1039.

4′-Amino-6′-benzoyl-4″-bromo-4-chloro-[1,1′:2′,1″-terphenyl]-3′,5′-dicarbonitrile (3h)

Yellow solid, yield: 92%; mp 250.2–250.8 °C (EA/PE); IR (KBr, cm^{-1}): ν 3441, 3332, 3225, 2216, 1670, 1638, 1437, 1244, 909, 846, 745; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.53 (d, J = 8.0 Hz, 2H), 7.45 (dd, J = 7.2 Hz and 7.2 Hz, 1H), 7.34 (d, J = 8.0 Hz, 2H), 7.28 (dd, J = 7.6 Hz and 7.6 Hz, 2H), 6.91 (d, J = 7.7 Hz, 2H), 6.85 (d, J = 8.0 Hz, 2H), 6.62 (d, J = 7.2 Hz, 2H), 5.39 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 192.5, 150.0, 148.2, 147.3, 134.0, 133.5, 133.4, 132.9, 132.0, 131.0, 130.7, 129.9, 128.5, 127.7, 127.2, 126.9, 122.7, 113.7, 112.7, 108.9, 98.2, 93.6; HR-MS (ESI) calcd for $C_{27}H_{15}BrClN_3O$ [(M + Na)$^+$]: 533.9985; found: 533.9982.

4′-Amino-6′-benzoyl-4″-chloro-4-methoxy-[1,1′:2′,1″-terphenyl]-3′,5′-dicarbonitrile (3i)

Yellow solid, yield: 90%; mp 244.4–245.0 °C (EA/PE); IR (KBr, cm^{-1}): ν 3449, 3336, 3236, 2225, 1671, 1634, 1442, 1264, 931, 843, 749; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.53 (d, J = 7.7 Hz, 2H), 7.36 (dd, J = 7.3 Hz and 7.3 Hz, 1H), 7.20 (dd, J = 7.5 Hz and 7.5 Hz, 2H), 7.16 (d, J = 8.1 Hz, 2H), 6.99 (d, J = 7.2 Hz, 2H), 6.58 (d, J = 6.8 Hz, 2H), 6.38 (d, J = 8.0 Hz, 2H), 5.36 (s, 2H), 3.53 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 193.1, 157.9, 150.0, 148.6, 147.6, 134.3, 134.2, 133.6, 133.4, 131.1, 130.0, 128.7, 128.3, 127.7, 125.8, 114.2, 113.2, 112.5, 98.3, 93.6, 54.1; HR-MS (ESI) calcd for $C_{28}H_{18}ClN_3O_2$ [(M + Na)$^+$]: 486.0985; found: 486.0991.

4′-Amino-6′-(4-bromobenzoyl)-4″-chloro-4-methoxy-[1,1′:2′,1″-terphenyl]-3′,5′-dicarbonitrile (3j)

Yellow solid, yield: 88%; mp 236.8–237.2 °C (EA/PE); IR (KBr, cm^{-1}): ν 3432, 3333, 3237, 2223, 1675, 1649, 1482, 1254, 941, 826, 750; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.39 (s, 4H), 7.17 (d, J = 8.8 Hz, 2H), 6.98 (d, J = 6.7 Hz, 2H), 6.57 (d, J = 6.7 Hz, 2H), 6.41 (d, J = 7.9 Hz, 2H), 5.35 (s, 2H), 3.56 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 192.9, 158.8, 150.7, 149.5, 147.7, 135.1, 134.2, 133.9, 131.9, 131.9, 130.7, 129.7, 129.1, 128.6, 126.4, 114.8, 113.8, 113.5, 99.4, 93.2, 55.0; HR-MS (ESI) calcd for $C_{28}H_{17}BrClN_3O_2$ [(M + Na)$^+$]: 564.0090; found: 564.0110.

4′-Amino-3,4″-dichloro-6′-(3-methylbenzoyl)-[1,1′:2′,1″-terphenyl]-3′,5′-dicarbonitrile (3k)

Yellow solid, yield: 93%; mp 214.9–215.2 °C (EA/PE); IR (KBr, cm^{-1}): ν 3452, 3323, 3236, 2212, 1664, 1648, 1478, 1251, 906, 819, 744; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.35 (s, 1H), 7.30 (d, J = 7.7 Hz, 1H), 7.25 (d, J = 7.5 Hz, 1H), 7.22–7.14 (dd, J = 9.2 Hz and 6.8 Hz, 3H), 6.99 (d, J = 7.7 Hz, 2H), 6.89 (d, J = 8.0 Hz, 1H), 6.81 (dd, J = 7.7 Hz and 7.7 Hz, 1H), 6.67 (s, 1H), 6.58 (d, J = 7.2 Hz, 1H), 5.39 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 193.5, 151.0, 149.1, 148.4, 138.6, 136.4, 135.4, 135.3, 135.0, 133.9, 133.7, 130.7, 130.6, 129.6, 129.1, 128.9, 128.7, 128.5, 127.9, 127.8, 126.9, 114.7, 113.8, 99.2, 94.6, 21.5; HR-MS

(ESI) calcd for $C_{28}H_{17}Cl_2N_3O$ [(M + Na)$^+$]: 504.0646; found: 504.0645.

4′-Amino-4″-bromo-3-chloro-6′-(3-methylbenzoyl)-[1,1′:2′,1″-terphenyl]-3′,5′-dicarbonitrile (3l)

White solid, yield: 92%; mp 227.5–228.7 °C (EA/PE); IR (KBr, cm^{-1}): ν 3434, 3331, 3238, 2223, 1670, 1643, 1449, 1216, 939, 825, 769; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.36 (s, 2H), 7.30 (d, J = 7.7 Hz, 1H), 7.26 (d, J = 7.6 Hz, 1H), 7.22–7.09 (m, 2H), 6.96–6.85 (m, 3H), 6.81 (dd, J = 7.6 Hz and 7.6 Hz, 1H), 6.68 (s, 1H), 6.58 (d, J = 7.1 Hz, 1H), 5.38 (s, 2H), 2.25 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 192.7, 150.3, 148.3, 147.6, 137.8, 135.6, 134.6, 134.2, 133.6, 133.0, 130.9, 130.1, 129.9, 128.9, 128.3, 128.1, 127.7, 127.1, 126.2, 122.9, 113.9, 113.0, 98.3, 93.9, 20.3; HR-MS (ESI) calcd for $C_{28}H_{17}BrClN_3O$ [(M + Na)$^+$]: 548.0141; found: 548.0148.

4′-Amino-4-chloro-4″-methyl-6′-(3-methylbenzoyl)-[1,1′:2′,1″-terphenyl]-3′,5′-dicarbonitrile (3m)

Yellow solid, yield: 89%; mp 214.6–215.4 °C (EA/PE); IR (KBr, cm^{-1}): ν 3456, 3338, 3235, 2213, 1662, 1639, 1419, 1276, 925, 825, 751; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.39 (s, 1H), 7.32 (d, J = 7.6 Hz, 1H), 7.27 (d, J = 7.3 Hz, 1H), 7.22–7.13 (m, 1H), 7.01 (d, J = 7.7 Hz, 2H), 6.93 (d, J = 7.3 Hz, 2H), 6.85 (d, J = 7.9 Hz, 2H), 6.66 (d, J = 7.4 Hz, 2H), 5.38 (s, 2H), 2.27 (s, 3H), 2.24 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 194.0, 151.1, 150.8, 148.1, 139.0, 138.6, 135.3, 135.1, 133.7, 133.5, 132.6, 132.0, 129.6, 129.2, 129.0, 128.5, 127.9, 127.1, 115.1, 114.0, 99.5, 93.9, 21.2, 21.1; HR-MS (ESI) calcd for $C_{29}H_{20}ClN_3O$ [(M + Na)$^+$]: 484.1193; found: 484.1193.

4′-Amino-6′-benzoyl-3″-bromo-3-methyl-[1,1′:2′,1″-terphenyl]-3′,5′-dicarbonitrile (3n)

Yellow solid, yield: 91%; mp 232.6–233.3 °C (EA/PE); IR (KBr, cm^{-1}): ν 3447, 3330, 3230, 2221, 1676, 1647, 1449, 1249, 969, 846, 740; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.51 (d, J = 7.1 Hz, 2H), 7.40 (d, J = 6.8 Hz, 1H), 7.32 (d, J = 7.7 Hz, 1H), 7.29–7.16 (m, 3H), 7.04 (dd, J = 7.3 Hz and 7.3 Hz, 1H), 6.99 (s, 1H), 6.72 (d, J = 7.1 Hz, 1H), 6.69 (s, 1H), 6.49 (s, 2H), 5.37 (s, 2H), 1.93 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 192.7, 149.8, 147.6, 147.2, 136.8, 136.4, 134.3, 133.2, 133.1, 131.3, 130.8, 130.4, 128.6, 128.4, 127.4, 127.4, 127.0, 126.8, 126.6, 121.0, 113.8, 112.9, 98.1, 93.6, 19.9; HR-MS (ESI) calcd for $C_{28}H_{18}BrN_3O$ [(M + Na)$^+$]: 514.0531; found: 514.0528.

4-Amino-2-benzoyl-3′-methyl-6-(thiophen-2-yl)-[1,1′-biphenyl]-3,5-dicarbonitrile (3o)

White solid, yield: 84%; mp 245.2–245.9 °C (EA/PE); IR (KBr, cm^{-1}): ν 3452, 3326, 3239, 2206, 1674, 1643, 1472, 1272, 932, 859, 709; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.51 (d, J = 8.2 Hz, 2H), 7.41 (dd, J = 6.9 Hz and 6.9 Hz, 1H), 7.25 (dd, J = 6.9 Hz and 6.9 Hz, 3H), 7.04–7.02 (m, 1H), 6.89–6.84 (m, 1H), 6.88 (dd, J = 7.5 Hz and 7.5 Hz, 2H), 6.54 (d, J = 11.6 Hz, 2H), 5.34 (s, 2H), 1.95 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 192.7, 149.9, 147.0, 142.3, 136.4, 135.0, 134.3, 133.6, 133.1, 130.5, 129.3, 129.1, 128.4, 128.2, 127.5, 127.4, 126.8, 126.6, 125.7, 114.2, 113.0, 105.6, 98.5, 93.3, 20.0; HR-MS (ESI) calcd for $C_{26}H_{17}N_3OS$ [(M + Na)$^+$]: 442.0990; found: 442.0989.

4′-Amino-6′-benzoyl-3″-chloro-3-methyl-[1,1′:2′,1″-terphenyl]-3′,5′-dicarbonitrile (3p)

Yellow solid, yield: 89%; mp 232.9–233.6 °C (EA/PE); IR (KBr, cm^{-1}): ν 3455, 3319, 3233, 2209, 1671, 1645, 1489, 1259, 903, 829, 752; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.52 (d, J = 7.9 Hz, 2H), 7.41 (dd, J = 7.4 Hz and 7.4 Hz, 1H), 7.25 (dd, J = 7.7 Hz and J = 7.7 Hz, 2H), 7.18 (d, J = 2.9 Hz, 1H), 7.11 (dd, J = 7.8 Hz and 7.8 Hz, 1H), 7.06 (s, 1H), 6.94 (d, J = 7.5 Hz, 1H), 6.76–6.64 (m, 2H), 6.53–6.42 (m, 2H), 5.34 (s, 2H), 1.93 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 192.8, 149.8, 147.8, 147.2, 136.6, 136.4, 134.3, 133.2, 133.1, 133.0, 130.4, 128.4, 127.9, 127.4, 127.3, 126.8, 126.6, 126.6, 113.8, 113.0, 98.1, 93.6, 19.9; HR-MS (ESI) calcd for $C_{27}H_{15}ClN_3O$ [(M + Na)$^+$]: 470.1036; found: 470.1034.

4′-Amino-3″-chloro-3-methyl-6′-(3-methylbenzoyl)-[1,1′:2′,1″-terphenyl]-3′,5′-dicarbonitrile (3q)

Yellow solid, yield: 91%; mp 206.9–207.6 °C (EA/PE); IR (KBr, cm^{-1}): ν 3447, 3328, 3239, 2226, 1668, 1645, 1471, 1250, 966, 824, 728; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.34 (s, 1H), 7.30 (d, J = 7.7 Hz, 1H), 7.24–7.04 (m, 5H), 6.94 (d, J = 7.4 Hz, 1H), 6.78–6.62 (m, 2H), 6.47 (d, J = 10.3 Hz, 2H), 5.35 (s, 2H), 2.23 (s, 3H), 1.94 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 193.3, 150.2, 148.2, 147.8, 137.8, 137.1, 136.8, 134.7, 134.4, 133.8, 133.5, 130.9, 129.1, 129.0, 128.9, 128.8, 128.3, 127.8, 127.7, 127.2, 127.0, 127.0, 126.4, 114.2, 113.4, 98.5, 94.1, 20.5, 20.4; HR-MS (ESI) calcd for $C_{29}H_{20}ClN_3O$ [(M + Na)$^+$]: 484.1193; found: 484.1191.

4′-Amino-4-methoxy-2″-methyl-6′-(3-methylbenzoyl)-[1,1′:2′,1″-terphenyl]-3′,5′-dicarbonitrile (3r)

White solid, yield: 88%; mp 196.2–197.1 °C (EA/PE); IR (KBr, cm^{-1}): ν 3435, 3330, 3235, 2224, 1661, 1639, 1459, 1249, 904, 853, 736; ^{1}NMR (400 MHz) δ (ppm): 7.37 (s, 1H), 7.31 (d, J = 7.4 Hz, 1H), 7.24–7.17 (m, 2H), 7.13 (dd, J = 7.5 Hz and 7.5 Hz, 1H), 6.97 (d, J = 7.4 Hz, 2H), 6.70 (d, J = 8.4 Hz, 2H), 6.60 (d, J = 7.2 Hz, 2H), 6.38 (d, J = 7.9 Hz, 2H), 5.29 (s, 2H), 3.69 (s, 3H), 3.54 (s, 3H), 2.23 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 193.5, 158.9, 157.7, 149.9, 149.8, 147.5, 137.6, 134.4, 134.2, 131.1, 130.1, 130.1, 128.9, 128.5, 127.5, 127.3, 126.5, 126.3, 114.6, 113.4, 112.8, 112.4, 109.2, 98.6, 92.9, 54.3, 54.1, 20.3; HR-MS (ESI) calcd for $C_{30}H_{23}N_3O_2$ [(M + Na)$^+$]: 480.1688; found: 480.1686.

4′-Amino-4″-chloro-3-methyl-6′-(3-methylbenzoyl)-[1,1′:2′,1″-terphenyl]-3′,5′-dicarbonitrile (3s)

Yellow solid, yield: 90%; mp 198.5–199.4 °C (EA/PE); IR (KBr, cm^{-1}): ν 3456, 3339, 3237, 2218, 1676, 1656, 1479, 1259, 921, 829, 729; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.34 (s, 1H), 7.30 (d, J = 7.7 Hz, 1H), 7.24–7.18 (m, 1H), 7.18–7.09 (m, 3H), 7.00 (d, J = 7.9 Hz, 2H), 6.76–6.65 (m, 2H), 6.50–6.42 (m, 2H), 5.37 (s, 2H), 2.22 (s, 3H), 1.93 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$)

δ (ppm): 193.2, 150.1, 148.3, 147.6, 137.5, 136.6, 134.4, 134.2, 133.7, 133.6, 130.7, 130.0, 128.9, 128.7, 127.6, 127.5, 127.0, 126.9, 126.2, 114.2, 113.2, 98.3, 93.7, 20.3, 20.2; HR-MS (ESI) calcd for $C_{29}H_{20}ClN_3O$ [(M + Na)$^+$]: 484.1193; found: 484.1187.

4-Amino-3′-chloro-2-(3-methylbenzoyl)-6-(thiophen-2-yl)-[1,1′-biphenyl]-3,5-dicarbonitrile (3t)

White solid, yield: 86%; mp 246.8–247.4 °C (EA/PE); IR (KBr, cm^{-1}): ν 3449, 3328, 3236, 2227, 1669, 1643, 1461, 1229, 946, 859, 746; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.43–7.34 (m, 4H), 7.28–7.24 (m, 1H), 7.07–7.02 (m, 1H), 6.92–6.86 (m, 1H), 6.80 (dd, J = 7.8 Hz and 7.8 Hz, 2H), 6.60–6.50 (m, 2H), 5.34 (s, 2H), 2.00 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 191.4, 149.7, 146.0, 142.1, 136.3, 134.6, 133.2, 132.8, 130.6, 130.2, 129.4, 129.1, 128.7, 128.3, 128.1, 127.5, 126.5, 126.4, 125.5, 113.9, 112.7, 98.4, 92.9, 19.8; HR-MS (ESI) calcd for $C_{26}H_{16}ClN_3OS$ [(M + Na)$^+$]: 476.0600; found: 476.0613.

4′-Amino-6′-benzoyl-3″,4,5″-trichloro-[1,1′:2′,1″-terphenyl]-3′,5′-dicarbonitrile (3u)

Yellow solid, yield: 93%; mp 197.6–198.5 °C (EA/PE); IR (KBr, cm^{-1}): ν 3448, 3334, 3235, 2221, 1677, 1646, 1468, 1253, 926, 825, 740; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.52 (d, J = 7.4 Hz, 2H), 7.45 (dd, J = 7.4 Hz and 7.4 Hz, 1H), 7.33–7.23 (m, 3H), 7.12–7.05 (m, 1H), 6.89 (d, J = 8.3 Hz, 1H), 6.84 (d, J = 7.8 Hz, 2H), 6.69 (d, J = 7.7 Hz, 2H), 5.36 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 192.3, 149.7, 147.3, 145.8, 135.0, 134.0, 133.6, 133.2, 132.4, 132.3, 131.6, 130.3, 128.7, 128.5, 127.7, 127.1, 126.4, 113.0, 112.6, 98.8, 94.3; HR-MS (ESI) calcd for $C_{27}H_{14}Cl_3N_3O$ [(M + Na)$^+$]: 524.0100; found: 524.0096.

4′-Amino-6′-benzoyl-3-methyl-4″-phenoxy-[1,1′:2′,1″-terphenyl]-3′,5′-dicarbonitrile (3v)

Yellow solid, yield: 88%; mp 184.5–185.3 °C (EA/PE); IR (KBr, cm^{-1}): ν 3432, 3321, 3229, 2218, 1672, 1645, 1456, 1249, 1202, 1171, 906, 834, 803; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): δ 7.56 (d, J = 6.8 Hz, 2H), 7.45 (d, J = 6.5 Hz, 1H), 7.34–7.18 (m, 5H), 7.06 (s, 1H), 6.94 (s, 2H), 6.85–6.74 (m, 2H), 6.71 (d, J = 7.0 Hz, 2H), 6.66 (s, 1H), 6.53 (s, 2H), 5.40 (s, 2H), 2.00 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 193.9, 156.7, 156.6, 150.8, 149.8, 148.0, 137.5, 137.3, 135.4, 134.7, 134.1, 131.5, 129.8, 129.7, 129.6, 129.4, 128.4, 128.2, 127.8, 127.7, 124.3, 123.3, 119.8, 119.7, 118.6, 114.9, 114.1, 99.3, 94.4, 21.0; HR-MS (ESI) calcd for $C_{34}H_{23}N_3O_2$ [(M + Na)$^+$]: 528.1688; found: 528.1692.

Methyl 4′-amino-3′,5′-dicyano-6′-(3-methoxybenzoyl)-3″-methyl-[1,1′:2′,1″-terphenyl]-4-carboxylate (3w)

White solid, yield: 84%; mp 229.9–230.5 °C (EA/PE); IR (KBr, cm^{-1}): ν 3443, 3328, 3221, 2219, 1675, 1648, 1453, 1250, 1213, 1171, 907, 832, 820; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.60 (d, J = 8.1 Hz, 2H), 7.27–7.21 (m, 1H), 7.17 (s, 1H), 7.13–7.07 (m, 2H), 7.03 (dd, J = 11.3, 5.1 Hz, 2H), 6.87 (d, J = 7.3 Hz, 4H), 5.42 (s, 2H), 3.79 (s, 3H), 3.76 (s, 3H), 2.21 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 193.4, 166.4, 159.8, 151.0, 150.7, 147.8, 140.0, 138.0, 136.4, 135.4, 130.9, 129.9, 129.8, 129.6, 129.0, 128.8, 128.2, 126.4, 122.8, 121.1, 114.9, 113.9, 113.2, 99.6, 94.1, 55.4, 52.0, 21.2; HR-MS (ESI) calcd for $C_{31}H_{23}N_3O_4$ [(M + Na)$^+$]: 524.1586; found: 524.1579.

4′-Amino-4-fluoro-6′-(3-methoxybenzoyl)-3″-methyl-[1,1′:2′,1″-terphenyl]-3′,5′-dicarbonitrile (3x)

Yellow solid, yield: 89%; mp 229.9–230.5 °C (EA/PE); IR (KBr, cm^{-1}): ν 3439, 3327, 3230, 2225, 1676, 1642, 1449, 1248, 1208, 1172, 918, 832, 815; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.24 (d, J = 8.1 Hz, 1H), 7.18 (s, 1H), 7.12 (dd, J = 7.9 Hz and 7.9 Hz, 2H), 7.08–6.99 (m, 2H), 6.88 (s, 2H), 6.74 (s, 2H), 6.62 (dd, J = 8.2 Hz and 8.2 Hz, 2H), 5.40 (s, 2H), 3.77 (s, 3H), 2.23 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 193.7, 161.8 (d, J = 246.8 Hz), 159.8, 151.0, 150.8, 148.1, 138.0, 136.5, 135.6, 132.6, 132.5, 131.0 (d, J = 3.6 Hz), 129.9, 129.6 (d, J = 9.8 Hz), 128.4, 128.1, 126.4, 122.8, 121.0, 114.9, 114.8 (d, J = 21.7 Hz), 114.0, 113.1, 99.5, 94.0, 55.4, 21.2; HR-MS (ESI) calcd for $C_{29}H_{30}FN_3O_2$ [(M + Na)$^+$]: 484.1437; found: 484.1432.

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